

# PATENT SPECIFICATION

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## (54) PROCESS FOR THE MANUFACTURE OF CONCENTRATED LIQUID DYEING PREPARATIONS OF LOW SALT CONTENT

—(71) We, CIBA-GEIGY A.G., a Swiss body corporate of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to a process for the manufacture of concentrated, liquid dyeing preparations of low salt content, especially preparations of water-soluble dyestuffs and optical brighteners. 5

10 Disperse dyestuffs, and above all water-soluble anionic and cationic dyestuffs and optical brighteners are usually separated out by salting-out of the reaction solution, for example with sodium chloride, potassium chloride or ammonium sulphate. In doing so, it is often very difficult to cause the dyestuff or optical brightener to separate out in a form which is easy to filter. In most cases, but not always, it is advantageous to effect the precipitation at approx. 70 to 80° C., and more rarely at the boil. By doing this, it is frequently possible to convert initially gelatinous precipitates into a crystalline or granular form. Apart from the precipitation temperature and the salt concentration, the pH value of the solution is sometimes also of importance as regards the character of the precipitate. For example, it sometimes happens that a precipitate which is easy to filter is only obtained over quite specific pH ranges. 15

20 Dyestuff salts or optical brightener salts which are still very soluble even in saturated salt solution must be isolated by, for example, evaporating the solution to dryness. 20

25 The dyestuffs or optical brighteners obtained by salting out and subsequent filtration, or by evaporating the coupling solution, condensation solution and/or neutralisation solution, in most cases have a high salt content. Dyeing preparations having a high salt content are frequently undesirable since, for example, they have too low a solubility, especially too low a solubility in cold water. Desalinating products containing salt, in practice, presents great difficulties, is expensive and in many cases leads to gelatinous pseudo-solutions which cannot be filtered. 25

30 Salting out, e.g. by dissolving and reprecipitating using organic solvents, is possible but complicated. Dialysis (artificial kidney) methods are also possible, but are very cumbersome and require large quantities of liquid. 30

35 Moreover, dyestuffs which have been isolated by salting out often contain low molecular coloured or colourless compounds, e.g. diazo and coupling components, monocondensates and hydrolysed sulphonic acid chlorides as impurities which are usually very difficult to isolate or at least must be isolated by chromatographic methods. 35

40 A process has now been found according to the present invention, which makes it possible to concentrate liquid dyeing preparations and reduce their salt content, especially to give impurity-free preparations of water-soluble dyestuffs and optical brighteners, in a simple manner so as to avoid all the abovementioned difficulties and disadvantages. According to the present invention, there is provided a process for concentrating, and reducing the salt content of, a liquid dyeing or optical brightening preparation which comprises passing a salt-containing solution or suspension of at least one dyestuff or optical brightening agent at least once, under pressure, over 40

a semipermeable membrane, which allows water and salt dissolved therein to pass through while retaining the dyestuff or optical brightening agent.

In contrast to the customary filtration, wherein solid particles are separated from liquids, the membrane-ultrafiltration process represents a selective molecular separation method.

The semi-permeable membranes act as molecular sieves, which retain dissolved substance at the membrane interface, with the molecular weight being the factor which decides retention or separation ("cut off levels"). Advantageously, membranes are employed which have a "cut off level" having at least 90% retention when they are subjected to a continuous ultrafiltration for 20 to 30 minutes. This membrane-ultrafiltration process is, of course, related to reverse osmosis wherein the molecular size of the substance or substances dissolved in the solution and of water must be in a certain size ratio to one another.

Semi-permeable membranes which can be used according to the present invention should ensure a high transmission of water and salts, such as sodium chloride, potassium chloride, ammonium sulphate, sodium phosphate, potassium sulphate, sodium acetate, and impurities, such as uncondensed or partially decomposed starting materials, which have a relatively low molecular weight. Additionally, however, they should also be sufficiently stable to suffer as little wear as possible in operation. These requirements are for example met by anisotropic, polymeric membranes, which consist of a very thin (for example 0.1 to 1.5 micron thick) layer having an extremely fine-pored texture (for example 2 to 100 Å diameter holes) on a much thicker layer (for example 50 to 250 microns thick) of an open-cell, porous plastic (sponge). The thin layer (skin) together with the porous substrate provide a combination of selectivity and high transmission, wherein blockages only occur rarely.

Semi-permeable membranes of cellulose acetate are preferred, but with these pH values of 3 to 9 should be maintained so as to avoid a degradation (hydrolysis) of the membrane as far as possible. Anisotropic (skin-layer) membranes of biologically inert, "non-cellulosic", synthetic polymers, such as nylon, but also poly-(vinyl isobutyl ether), poly-(ethyl acrylate), poly-tetrahydrofuran, poly-(triallyl phosphate), poly-(vinyl methyl ketone) and cellulose di- or tri-acetate, are very resistant because of their thermal, chemical and physical properties. They generally withstand temperatures of up to 200° C. and can be exposed to acids, alkali or oxidising agents without suffering damage. These membranes show a "cut off level" of molecular weight 300 to 10,000. For the process according to the present invention, membranes with a "cut off level" of molecular weight 400 to 1000 are particularly suitable. They permit the permeation of water, optionally mixed with organic solvents and dissolved substances, which because of their molecular sizes lie below the cut off level, at high speeds per unit area and at relatively low pressures. According to the invention, pressures of 3 to 100, and preferably 20 to 50 atmospheres generally suffice. The pressure can, for example, be exerted by means of compressed air or of a pump.

Naturally the cut off level must be such as to retain substantially all of the dyestuff or optical brightener; it will, of course, be appreciated that the process of this invention will only work satisfactorily if the molecular weight of the dyestuff is higher than that of the salts but this is nearly always the case.

In an ultrafiltration pass, the salting-out effect can be up to 70 per cent or more, without losses of dyestuff. During this, the volume of the solution of the retained substances above the membrane correspondingly decreases and the concentration of the retained particles increases. If a further reduction in the salts and other substances of low molecular weight is desired, this can be achieved without difficulties, after diluting the retained solution or suspension with water, preferably to the initial volume, by repeating the process once or several times. The ultrafiltration can also be carried out continuously, by matching the speed of supply of the water to the speed of removal of the ultrafiltrate. Salting-out and purifying effects of up to 95%, or, if desired, even up to 99%, that is to say until the ultrafiltrate is free of undesired substances, can be achieved discontinuously and continuously in this simple manner.

Possible dyestuffs to which the process of this invention is applicable include disperse dyestuffs and, above all, water-soluble anionic and cationic dyestuffs, in particular monoazo, diazo or polyazo dyestuffs, formazane, anthraquinone, nitro, methine, styryl, azastyryl, naphthoperinone, quinophthalone or phthalocyanine dyestuffs.

The water-soluble anionic dyestuffs which preferably are used according to the present invention, are especially the alkali salts or ammonium salts of the so-called acid wool dyestuffs, of the reactive dyestuffs or of the substantive cotton dyestuffs of

the azo, anthraquinone and phthalocyanine series. Possible azo dyestuffs are preferably metal-free and metallisable monoazo and disazo dyestuffs which contain one or more sulphonic acid groups, monoazo, disazo and formazane dyestuffs which contain a heavy metal, particularly copper, chromium or cobalt, and metallised monoazo dyestuffs which contain 2 molecules of azo dyestuff bonded to one metal atom. As anthraquinone dyestuffs 1-amino-4-arylamino-anthraquinone-2-sulphonic acids should especially be mentioned, and as phthalocyanine dyestuffs, sulphonated copper phthalocyanines or phthalocyanine-arylamides should especially be mentioned.

The water-soluble basic dyestuffs include the customary salts and metal halide double salts, for example zinc chloride double salts, of the known cationic dyestuffs, especially of the methine or azamethine dyestuffs, which contain the indolinium, pyrazolium, imidazolium, triazolium, tetrazolium, oxadiazolium, thiodiazolium, oxazolium, thiazolium, pyridinium, pyrimidinium, and pyrazinium ring.

The heterocyclic structures mentioned can optionally be substituted and/or condensed with aromatic rings. Further, cationic dyestuffs of the diphenylmethane, triphenylmethane, oxazine, thiazine and 1,2-propane series can also be used, as can dyestuff salts of the arylazo and anthraquinone series having an external onium group.

Optical brighteners to which the process of this invention are applicable include disperse brighteners and above all water-soluble anionic and cationic optical brighteners. They can belong to any desired classes of brighteners, in particular stilbene compounds, such as 4,4' - bis - triazinylaminostilbene - sulphonic acids, stilbylnaphthotriazolesulphonic acids, 4,4' - bis - benzoylaminostilbene - sulphonic acids or 4,4' - bis - triazolylstilbene - sulphonic acid, also coumarines, such as derivatives of the 3 - aryl - 7 - subst. - amino - coumarines or benzocoumarines, and also pyrazines, such as 3,5-dialkylamino-pyrazine-2,6-dicarboxylic acid alkylamides or arylamides, pyrazolines, such as 1,3-diphenylpyrazolines or 1,3,5-triphenyl-pyrazolines, oxazine compounds, such as 3,3'-dialkyloxacyanines or 3,3',5,5'-tetraalkyloxacyanines, or the acid salts of these compounds, dibenzoxazolyl or dibenzimidazolyl compounds and naphthalic acid imides.

The starting solution or suspension used for the manufacture of the preparations according to the process of this invention is appropriately a slurry of the moist press or filter cake of dyestuffs or optical brighteners with varying contents of undesired dissolved substances such as dissolved inorganic salts, in water. In cases where, for example, the coupling product or condensation product cannot be salted out or can only be salted out with extreme difficulty, the coupling solution, condensation solution or neutralisation solution can also be used directly. Advantageously, starting solutions or suspensions which contain 2 to 50% and especially 10 to 30% by weight of dyestuff or optical brightener are used.

Surprisingly, no absorption or deposition of the large dyestuff molecules on the surface of the semi-permeable membrane takes place during the ultrafiltration of dyestuffs or optical brighteners, provided the viscosity of the solution or suspension is so chosen that it can be moved by a pump without difficulties. Such a deposition would render the membrane only slightly permeable to impermeable, which would make a desalination very difficult and would additionally require very high pressures.

According to the process of the invention, the solutions or suspensions of dyestuffs or optical brighteners are desalinated and simultaneously freed of impurities, which molecular size lie below the cut off level, and then they can be concentrated to a content of dyestuff or optical brightener of 10%, and advantageously 20 to 50%, by weight. When using water-soluble dyestuffs or optical brighteners, clear solutions are in most cases obtained. These concentrated solutions of low salt content surprisingly show no tendency to form jelly-like pseudo-solutions, and are storage-stable, directly ready to use and easily soluble in cold water, often without any addition of auxiliaries which confer solubility in water. In order to make the preparations stable for storage for a long period, it may be advantageous to add water-soluble auxiliaries such as urea, dextrin, glucose and diethylene glycol to the concentrates which have been obtained.

The resulting concentrated, liquid dyeing preparations of low salt content can, if desired, be concentrated further, for example in vacuo, or can even be evaporated to dryness. Easily soluble products which are free of the hitherto customary fillers, can thereby be obtained in an extremely simple manner.

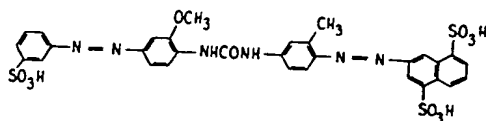
Thus it is possible by the process according to the invention in a simple manner to produce substances which are pure enough for photographic and drawing materials such as are used for pressure copying. Dyestuffs for photographic purposes, e.g. dyestuffs of the azo series used for photographic prints, must be practically completely free

from salts and low molecular impurities such as starting materials and decomposition products.

The Examples which follow further illustrate the present invention

Example 1.

360 g of moist dyestuff press cake, containing 120 g of dyestuff of the formula



are suspended in 1500 ml of water, and the dyestuff suspension containing about 15% of sodium chloride is continuously ultra-filtrated at room temperature, whilst constantly supplying an amount of water corresponding to the ultrafiltrate, and using a semi-permeable cellulose acetate membrane having a "cut off level" of molecular weight 400, and a pressure of 35 kg/cm<sup>2</sup> (500 lb per square inch). After removing 95% of the theoretical amount of sodium chloride (measured from salt content of the ultrafiltrate) from the original suspension, without loss of dyestuff, which is achieved by passage of 4000 ml of water, the supply of water is stopped, and after concentrating the dyestuff solution to a volume of 600 ml the ultrafiltration is stopped.

The dyestuff solution thus obtained can be concentrated in vacuo to a volume of 300 ml, whereby an intensely coloured and directly usable dyeing preparation is obtained, which is stable, with the dissolved dyestuff showing no tendency to separate out. To obtain a commercial preparation which is storage stable for a long period, advantageously 5% by weight of urea or diethylene glycol are added to the concentrate.

Pouring the preparation into warm water and adding the auxiliaries customary in dyeing yields a directly usable liquor for dyeing cellulose fibres, especially paper, in yellow colour shades.

If in the above Example, the dyestuff of the press cake is replaced by corresponding amounts of the substantive dyestuffs indicated in Table I below, column 2, and in other respects the procedure indicated in the Example is followed, directly ready-to-use and storage-stable dyeing preparations are again obtained, which dye cellulose fibres in the colour shades indicated in the last column.

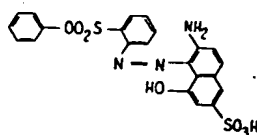
TABLE I

Example No.	Dyestuff	Colour shade on cellulose fibres
2		blue
3		scarlet
4		blue
5		brown
6		yellow
7		yellow
8		orange
9		brown

Concentration of the dyeing preparations, obtainable according to Examples 1 to 9, in vacuo to a volume of 300 ml or to dryness, yields extremely easily water-soluble dyestuff preparations of low salt content.

#### Example 10.

150 g of the dyestuff of the formula



which has been isolated by salting-out, and dried, are dissolved in 3000 ml of water at 70° C., and the solution containing about 10% of sodium chloride is cooled to room temperature and ultrafiltered by means of a semi-permeable polyamide membrane with a "cut off level" of molecular weight 450, and a pressure of 10 kg/cm<sup>2</sup>, and is simultaneously concentrated to a volume of 250 ml. A concentrated, stable, directly ready-to-use dyestuff solution is thus obtained. After pouring the preparation into water and adding the auxiliaries customary in dyeing, a directly usable liquor for dyeing wool in red colour shades is obtained.

If in the above Example, the dyestuff is replaced by corresponding amounts of the dyestuffs indicated in Table II below, column 2, and in other respects the procedure indicated in the Example is followed, directly ready-to-use and storage-stable dyeing preparations are again obtained, which dye wool and synthetic polyamide in the colour shades indicated in the last column of the table.

TABLE II

Example No.	Dyestuff	Colour shade on wool and synthetic polyamide
11		yellow
12	<p>2:1 cobalt complex</p>	yellow
13		green

TABLE II (Continued)

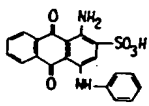
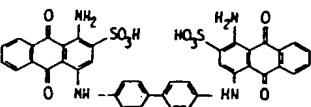
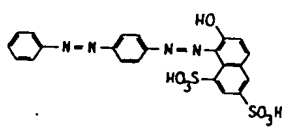
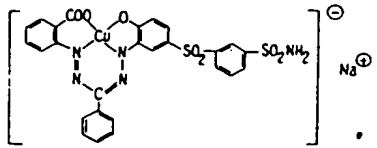
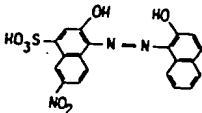
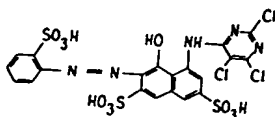
Example No.	Dyestuff	Colour shade on wool and synthetic polyamide
14	4,4'-bis-(o-diazophenyl-sulphonyloxy)-diphenylmethane $\xrightarrow{\quad}$ 1-phenyl-3-methyl-5-aminopyrazole-4'-sulphonic acid (2 equivalents)	yellow
15	4,4'-bis-(o-diazophenyl-sulphonyloxy)-diphenylmethane $\xrightarrow{\quad}$ 2-aminonaphthalene-5-sulphonic acid (2 equivalents)	orange
16	4,4'-bis-(o-diazophenyl-sulphonyloxy)-diphenylmethane $\xrightarrow{\quad}$ 2-amino-8-hydroxynaphthalene-6-sulphonic acid (2 equivalents, acid)	red
17		blue
18		blue
19		scarlet
20		blue

TABLE II (Continued)

Example No.	Dyestuff	Colour shade on wool and synthetic polyamide
21		black after chroming

## Example 22.

900 g of a moist press cake, which contains 500 g of the dyestuff of the formula



- 5 are introduced into 5000 ml of water, whilst stirring, and the resulting dyestuff solution is continuously ultrafiltered at room temperature with constant supply of an amount of water corresponding to the ultrafiltrate, and using a semi-permeable cellulose acetate membrane with a "cut off level" of molecular weight 500 and a pressure of 25 kg/cm<sup>2</sup>; after a passage of 10000 ml of water no chloride ions or not-acylated starting material are detectable in the ultrafiltrate. Thereafter, the supply of water is switched off and the dyestuff solution is concentrated to a volume of 1000 ml. The dyeing preparation thus obtained is very stable and directly ready to use. On stirring the preparation into water, and after adding thickeners and the auxiliaries which are customary in dyeing, a printing paste for printing natural or regenerated cellulose fibres is obtained.
- 10 If instead of the abovementioned press cake, the coupling solution of the dyestuff of the above formula, obtained by coupling diazotised 1-aminobenzene-2-sulphonic acid with 1-(2,4,5-trichloropyrimidin-2-ylamino)-8-hydroxynaphthalene-3,6-disulphonic acid, is used, and in other respects the procedure indicated in the Example is followed, a dyeing preparation with similarly good properties is obtained.
- 15 If, in the above Example, the dyestuff in the press cake is replaced by corresponding amounts of the reactive dyestuffs indicated in Table III, below, column 2, and in other respects the procedure indicated in the Example is followed, directly ready-to-use and storage-stable dyeing preparations are again obtained, which dye natural or regenerated cellulose in the colour shades indicated in the last column of the table.
- 20
- 25

TABLE III

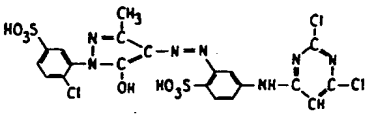
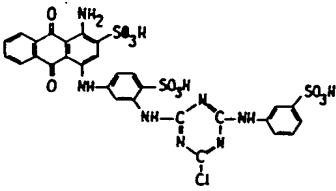
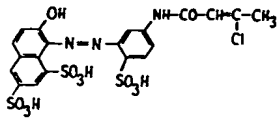
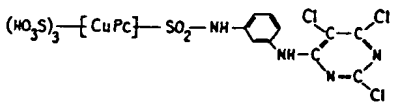
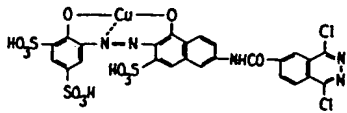
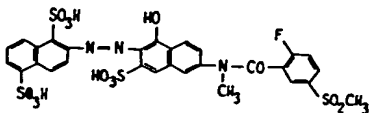
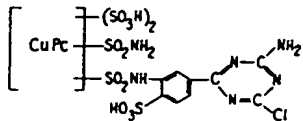
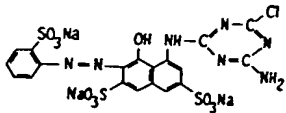
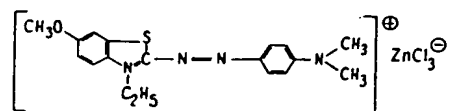
Example No.	Dyestuff	Colour shade on natural and regenerated cellulose
23		greenish-tinged yellow
24		blue
25		orange
26	 (wherein CuPc denotes the copper phthalocyanine radical)	turquoise

TABLE III (Continued)

Example No.	Dyestuff	Colour shade on natural and regenerated cellulose
27		claret
28		orange
29		turquoise
30		red

## Example 31.

360 g of moist press cake, which contains 120 g of the dyestuff of the formula



are introduced into 2000 ml of water, whilst stirring, and the resulting dyestuff solution is continuously ultrafiltered, with constant supply of an amount of water corresponding to the ultrafiltrate, and using a semi-permeable cellulose triacetate membrane having a "cut off level" of molecular weight 1000, and a pressure of 10 kg/cm<sup>2</sup>, until chloride ions are no longer detectable in the ultrafiltrate. Thereafter, the supply of water is switched off and the dyestuff solution is concentrated to a volume of 250 ml.

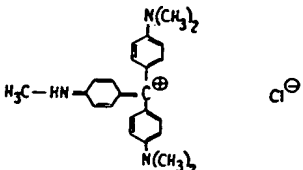
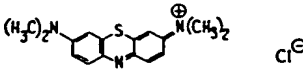
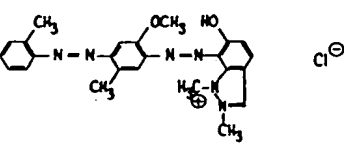
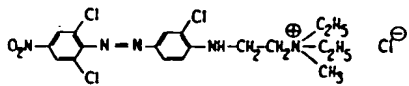
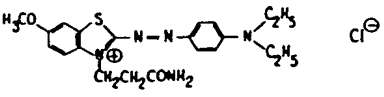
The dark blue, concentrated dyestuff solution manufactured in this manner is

storage-stable and directly ready to use. On pouring the preparation into a 100-fold amount of cold or warm water and adding auxiliaries which are customary in dyeing, a directly usable liquor for dyeing acrylonitrile fibres from a short bath is obtained.

5 If, in the above Example, the dyestuff in the press cake is replaced by corresponding amounts of the cationic dyestuff salts indicated in Table IV below, column 2, and in other respects the procedure indicated in the Example is followed, directly ready-to-use and storage-stable dyeing preparations are again obtained, which dye poly-acrylonitrile fibres in the colour shades indicated in the last column of the table.

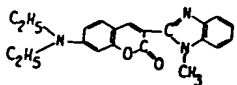
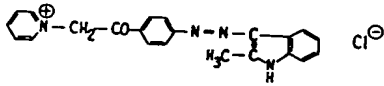
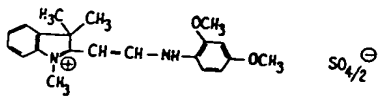
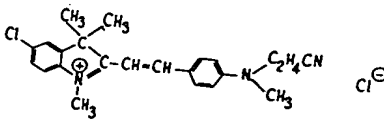
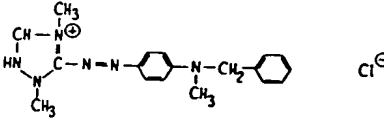
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TABLE IV

Example No.	Cationic dyestuff salts	Colour shade on polyacrylonitrile fibres
32		violet
33		blue
34		scarlet
35		orange
36		blue

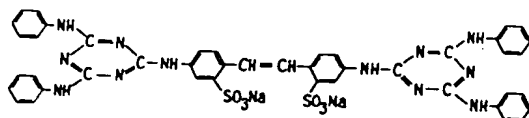
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TABLE IV (Continued)

Example No.	Cationic dyestuff salts	Colour shade on polyacrylonitrile fibres
37		brilliant yellow
38		yellow
39		yellow
40		pink
41		red

## Example 42.

1.5 kg of moist filter cake, containing 450 g of optical brightener of the formula



are introduced into 5000 ml of water, whilst stirring, and the resulting brightener suspension is ultrafiltered at room temperature, using a semi-permeable membrane of cellulose diacetate having a "cut off level" of molecular weight 500, and a pressure of 20 kg/cm<sup>2</sup>. After removing 5000 ml of ultrafiltrate, the brightener suspension is diluted with 5000 ml of water and again ultrafiltered.

The concentrated optical brightener preparation obtained in this manner is storage-stable and directly ready to use. On pouring a calculated amount of the preparation into water and adding auxiliaries which are customary in dyeing, a directly usable liquor for brightening natural and regenerated cellulose is obtained.

5 If, in the above Example, the optical brightener is replaced by corresponding amounts of the optical brighteners indicated in Table V below, column 2, and in other respects the procedure indicated in the Example is followed, directly ready-to-use and storage-stable brightener preparations are again obtained.

5

TABLE V

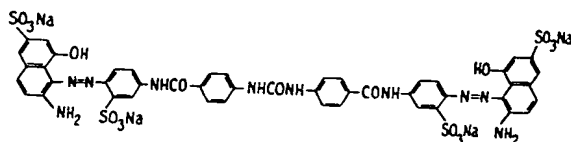
Example No.	Optical brightener
43	
44	
45	
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48	

TABLE V (Continued)

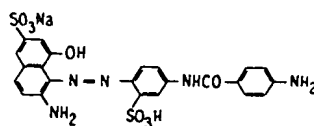
Example No.	Optical brightener
49	
50	
51	

## Example 52.

100 g of moist filter cake, containing 36 g of the dyestuff of the formula



5 are introduced in 3500 ml of water whilst stirring and the resulting dyestuff suspension containing 8 g of the dyestuff base of the formula



10 is continuously ultrafiltered with constant supply of an amount of water corresponding to the ultrafiltrate at room temperature, using a semi-permeable membrane of cellulose acetate having a "cut off level" of molecular weight 10,000 and a pressure of 7

kg/cm. After a passage of 18,000 ml of water no dyestuff base of the above formula is detectable in the ultrafiltrate, identified by using a thin layer chromatographic analyse. Every 15 minutes 400 ml of ultrafiltrate passed through the semi-permeable membrane. Thereafter, the supply of water is switched off and the dyestuff solution is concentrated to a volume of 500 ml, which concentrate has been evaporated in vacuo to dryness, yielding an extremely pure, highly concentrated, easily water-soluble dyestuff preparation, which can directly be used for photographic prints.

WHAT WE CLAIM IS:—

1. Process for concentrating, and reducing the salt content of, a liquid dyeing or optical brightening preparation which comprises passing a salt-containing solution or suspension of at least one dyestuff or optical brightening agent at least once, under pressure, over a semi-permeable membrane, which allows water and salt dissolved therein to pass through while retaining the dyestuff or optical brightening agent.

2. Process according to claim 1 in which the dyestuff is a water-soluble anionic dyestuff.

3. Process according to claim 1 or 2 in which the preparation is a solution resulting from a coupling, condensation or neutralisation reaction.

4. Process according to any one of claims 1 to 3 in which the preparation is a slurry of a moist press or filter cake of at least one dyestuff or optical brightener in water.

5. Process according to any one of the preceding claims in which the semi-permeable membrane is of cellulose acetate.

6. Process according to any one of claims 1 to 5 in which the semi-permeable membrane has a molecular weight "cut off" of 300 to 10,000.

7. Process according to claim 6 in which the semi-permeable membrane has a molecular weight "cut off" of 400 to 1000.

8. Process according to any one of the preceding claims in which the preparation is an aqueous solution or suspension which contains 2 to 50% by weight of dyestuff or optical brightener.

9. Process according to any one of the preceding claims in which a pressure of 3 to 100 atmospheres is used.

10. Process according to claim 1 substantially as hereinbefore described.

11. Process according to claim 1 substantially as described in any one of Examples 1 to 7, 11 to 28, 31 to 36, 38, 39, 42 and 43.

12. Process according to claim 1 substantially as described in any one of Examples 8, 9, 10, 29, 30, 37, 40, 41 and 44 to 52.

13. A liquid dyeing or optical brightening preparation whenever obtained by a process as claimed in any one of claims 1 to 12.

14. A preparation according to claim 13 which is concentrated to give a 20 to 50% by weight concentration of dyestuff or optical brightening agent.

15. A preparation according to claim 13 which is concentrated to dryness.

16. A preparation according to any one of claims 13 to 15 whenever obtained by a process as claimed in any one of claims 1 to 5 and 11

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